

Alkynes

An **alkyne** is a hydrocarbon that contains a carbon–carbon triple bond. Acetylene, $\text{H}-\text{C}\equiv\text{C}-\text{H}$, the simplest alkyne, was once widely used in industry as a starting material for the preparation of acetaldehyde, acetic acid, vinyl chloride, and other high-volume chemicals, but more efficient routes to these substances using ethylene as starting material are now available. Acetylene is still used in the preparation of acrylic polymers, but is probably best known as the gas burned in high-temperature oxy–acetylene welding torches.

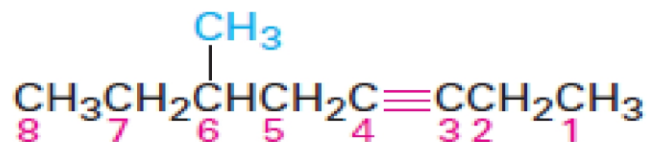
In addition to simple alkynes with one triple bond, research is also being carried out on *Polyynes*—linear carbon chains of *sp*-hybridized carbon atoms. Polyynes with up to eight triple bonds have been detected in interstellar space, and evidence has been presented for the existence of *carbyne*, an allotrope of carbon consisting of repeating triple bonds in long chains of indefinite length. The electronic properties of polyynes are being explored for potential use in nanotechnology applications.



A polyyne detected in interstellar space

Naming Alkynes

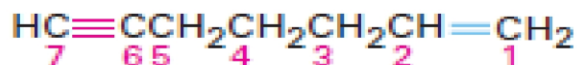
Alkyne nomenclature follows the general rules for hydrocarbons. The suffix *-yne* is used, and the position of the triple bond is indicated by giving the number of the first alkyne carbon in the chain. Numbering the main chain begins at the end nearer the triple bond so that the triple bond receives as low a number as possible.



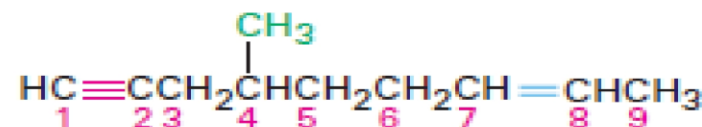
Begin numbering at the end nearer the triple bond.

6-Methyl-3-octyne
(New: **6-Methyloct-3-yne**)

Compounds with more than one triple bond are called diynes, triynes, and so forth; compounds containing both double and triple bonds are called enynes (not ynenes). Numbering of an enyne chain starts from the end nearer the first multiple bond, whether double or triple. When there is a choice in numbering, double bonds receive lower numbers than triple bonds. For example:

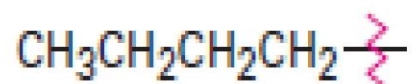


1-Hepten-6-yne
(New: **Hept-1-en-6-yne**)



4-Methyl-7-nonen-1-yne
(New: **4-Methylnon-7-en-1-yne**)

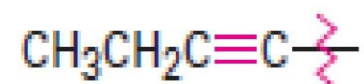
As with alkyl and alkenyl substituents derived from alkanes and alkenes, respectively, alkynyl groups are also possible.



Butyl
(an alkyl group)



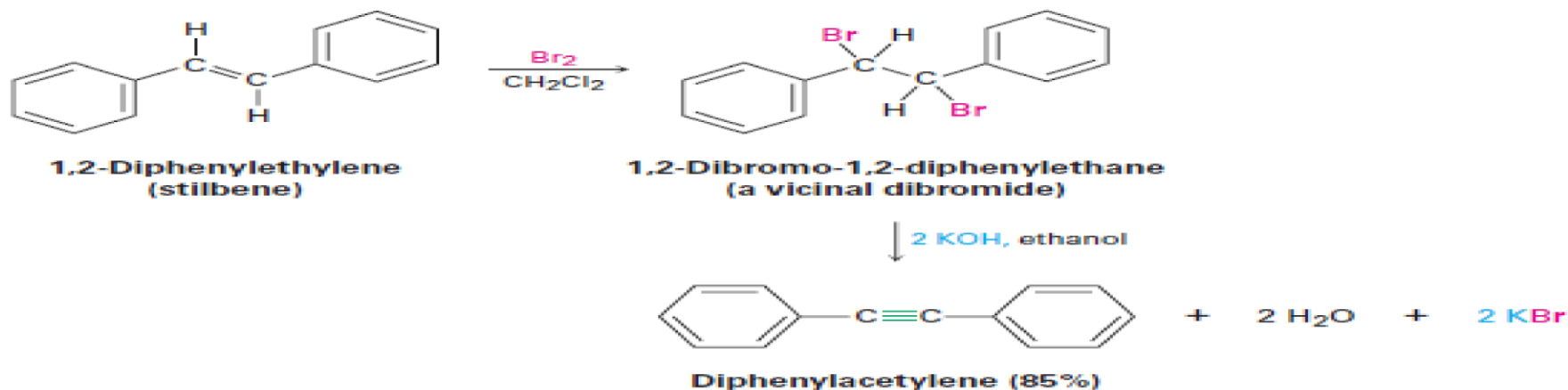
1-Butenyl
(a vinylic group)
(New: But-1-enyl)



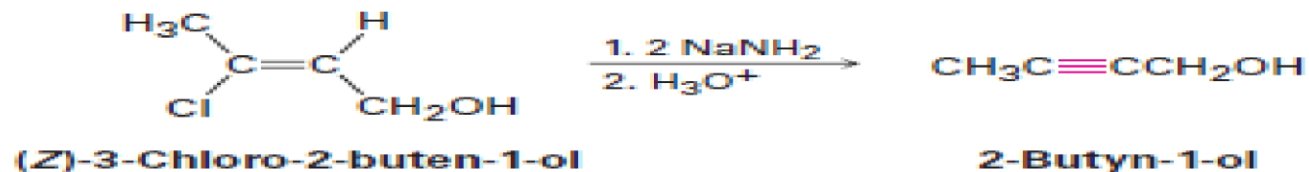
1-Butynyl
(an alkynyl group)
(New: But-1-ynyl)

Preparation of Alkynes: Elimination Reactions of Dihalides

Alkynes can be prepared by the elimination of HX from alkyl halides in a similar manner as alkenes. Treatment of a 1,2-dihaloalkane (a *vicinal* dihalide) with an excess amount of a strong base such as KOH or NaNH₂ results in a twofold elimination of HX and formation of an alkyne. As with the elimination of HX to form an alkene, the starting vicinal dihalides are themselves readily available by addition of Br₂ or Cl₂ to alkenes. Thus, the overall halogenation/dehydrohalogenation sequence makes it possible to go from an alkene to an alkyne. For example, diphenylethylene is converted into diphenylacetylene by reaction with Br₂ and subsequent base treatment.



The twofold dehydrohalogenation takes place through a vinylic halide intermediate, which suggests that vinylic halides themselves should give alkynes when treated with strong base. (*Remember: A vinylic substituent is one that is attached to a double-bond carbon.*) This is indeed the case. For example:



Reactions of Alkynes: Addition of HX and X₂

You might recall that a carbon–carbon triple bond results from the interaction of two *sp*-hybridized carbon atoms. The two *sp* hybrid orbitals of carbon lie at an angle of 180° to each other along an axis perpendicular to the axes of the two unhybridized 2*py* and 2*pz* orbitals. When two *sp*-hybridized carbons approach each other, one *sp*–*sp* σ bond and two *p*–*p* π bonds are formed. The two remaining *sp* orbitals form bonds to other atoms at an angle of 180° from the carbon–carbon bond. Thus, acetylene is a

linear molecule with $\text{H}-\text{C}\equiv\text{C}$ bond angles of 180° (**Figure 9-1**). The length of the $\text{C}\equiv\text{C}$ bond is 120 pm, and its strength is approximately 965 kJ/mol (231 kcal/mol), making it the shortest and strongest known carbon–carbon bond

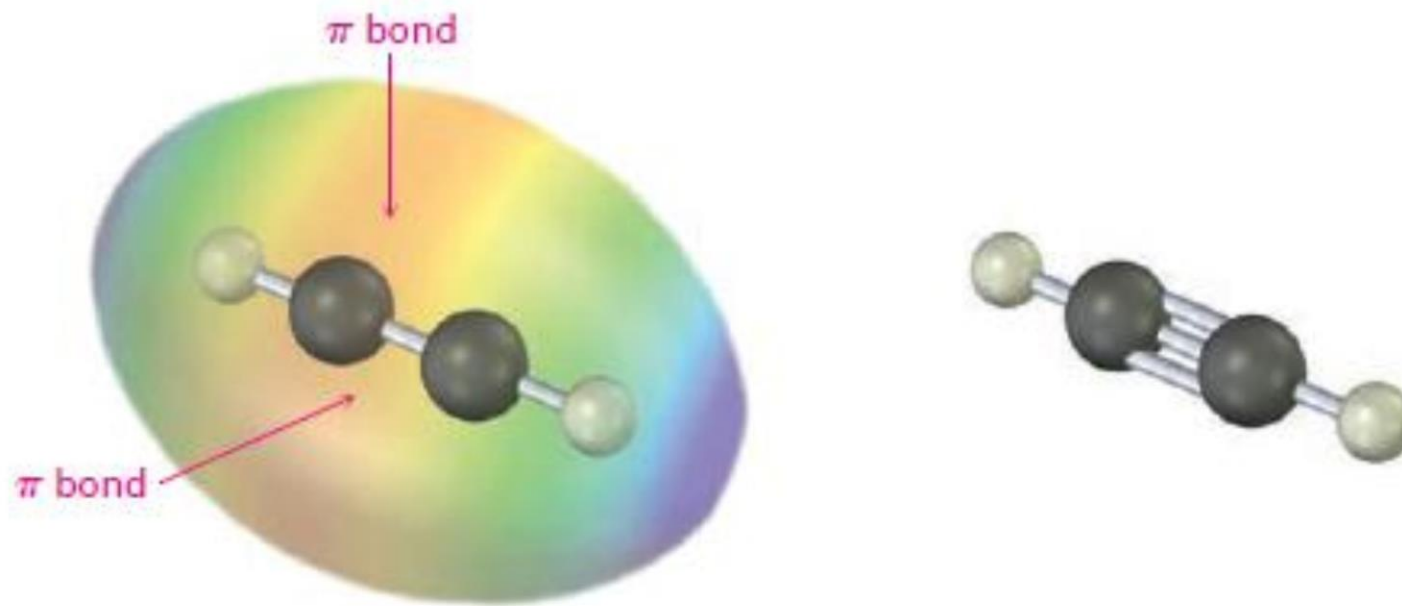
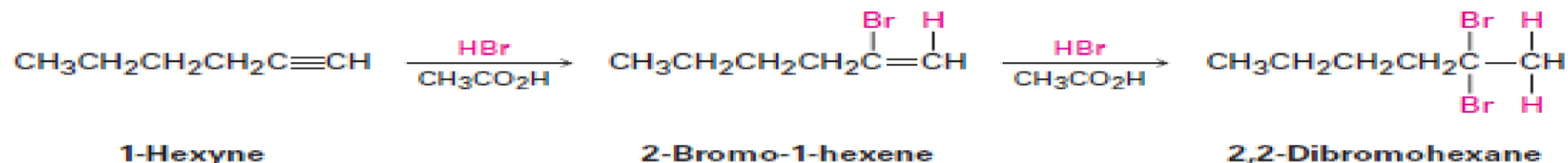


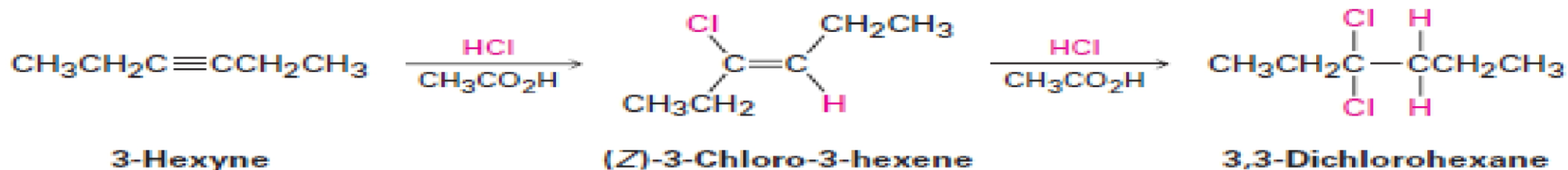
Figure 9-1 The structure of acetylene, $\text{H}-\text{C}\equiv\text{C}-\text{H}$. The $\text{H}-\text{C}\equiv\text{C}$ bond angles are 180° , and the $\text{C}\equiv\text{C}$ bond length is 120 pm. The electrostatic potential map shows that the π bonds create a negative belt around the molecule.

As a general rule, electrophiles undergo addition reactions with alkynes much as they do with alkenes. Take the reaction of alkynes with HX, for instance. The reaction often can be stopped with the addition of 1 equivalent of HX, but reaction with an excess of HX leads to a dihalide product. For example, reaction of 1-hexyne with 2 equivalents of HBr yields 2,2-dibromohexane. As the following examples indicate, the regiochemistry of addition follows Markovnikov's rule, with halogen adding to the more highly substituted side of the alkyne bond and hydrogen adding to the less highly substituted side. Trans stereochemistry of H and X normally, although not always, occurs in the product.

HBr addition

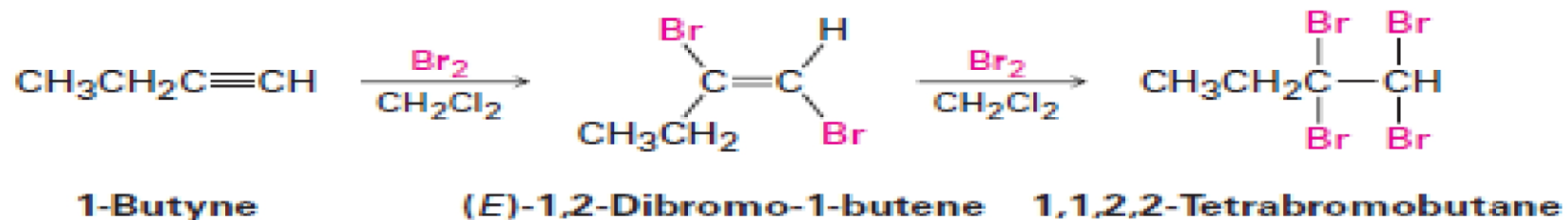


HCl addition

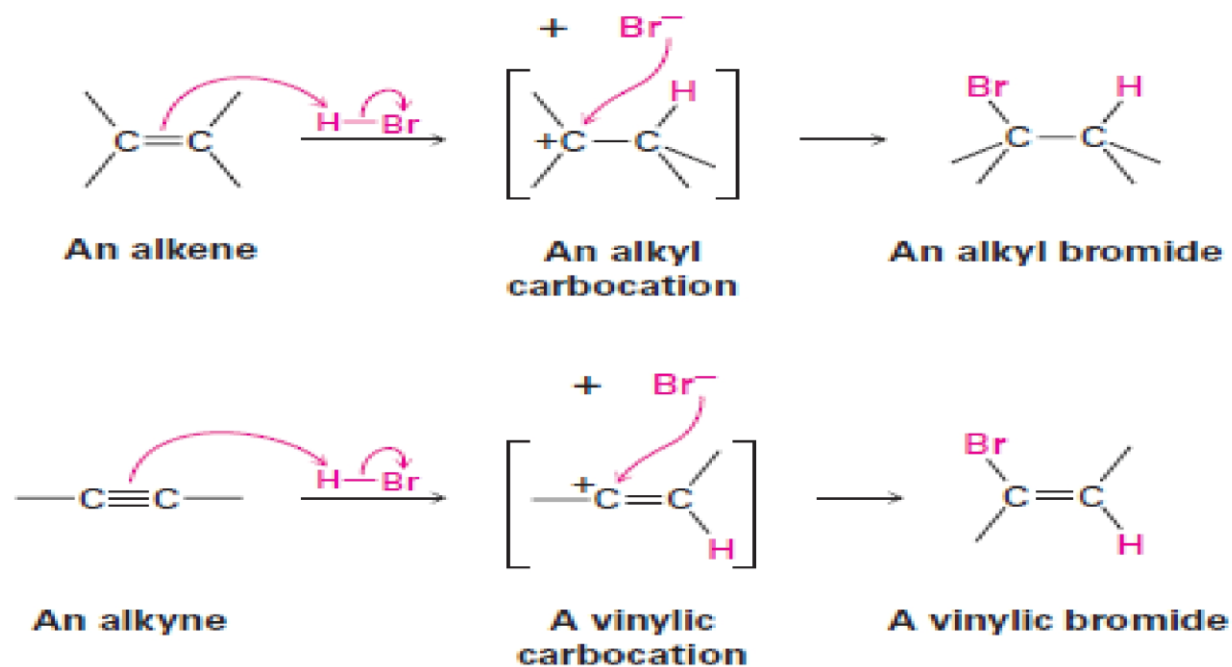


Bromine and chlorine also add to alkynes to give addition products, and trans stereochemistry again results.

Br₂ addition



The mechanism of alkyne addition is similar but not identical to that of alkene addition. When an electrophile such as HBr adds to an alkene, the reaction takes place in two steps and involves an alkyl carbocation intermediate. If HBr were to add by the same mechanism to an *alkyne*, an analogous *vinyllic* carbocation would be formed as the intermediate.

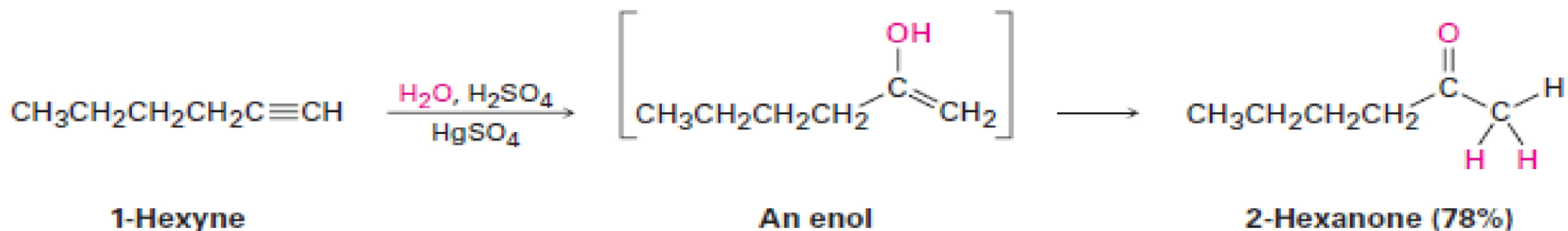


Hydration of Alkynes

Like alkenes, alkynes can be hydrated by either of two methods. Direct addition of water catalyzed by mercury (II) ion yields the Markovnikov product, and indirect addition of water by a hydroboration–oxidation sequence yields the non-Markovnikov product.

Mercury (II)-Catalyzed Hydration of Alkynes

Alkynes don't react directly with aqueous acid but will undergo hydration readily in the presence of mercury (II) sulfate as a Lewis acid catalyst. The reaction occurs with Markovnikov regiochemistry, so the -OH group adds to the more highly substituted carbon and the -H attaches to the less highly substituted one.



Interestingly, the actual product isolated from alkyne hydration is not a vinylic alcohol, or **enol** (*ene* + *ol*), but is instead a ketone. Although the enol is an intermediate in the reaction, it immediately rearranges into a ketone by a process called *keto–enol tautomerism*. The individual keto and enol forms are said to be **tautomers**, a word used to describe two isomers that undergo spontaneous interconversion accompanied by the change in position of hydrogen. With few exceptions, the keto–enol tautomeric equilibrium lies on the side of the ketone; enols are almost never isolated.

